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SCFMO calculations of the π electron energy states of some halo-substituted benzaldehydes and benzoyl halides

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π-electron energy states of benzaldehyde, para-, meta- and ortho-chloro and bromo benzaldehydes, benzoyl chloride and benzoyl bromide have been calculated and the nature of the different excited states in benzaldehyde and halo-substituted benzladehydes has been investigated. For benzaldehyde, the first excited state may be correlated with the ψ -state of benzene. But its other higher excited states and the different excited states of halo-substituted benzaldehydes can hardly be correlated with those of benzene and the charge transfer states between the substitutents and the benzene molecule.

1. Introduction

It is well known that the ultraviolet absorption spectra of benzaldehyde, substituted benzaldehydes and benzoyl halides in solutions and in vapour phase in most cases consist of three systems of bands in the regions 2800Å, 2400Å and 2100Å. The first two systems have generally been correlated with the benzenoid α- and p-bands respectively but Sashidhar (1971) pointed out that though the 2800Å band system may be a shifted band of benzene, the band system at the 2400Å region might be due to an intramolecular charge transfer.

In order to investigate the above points, calculations have been made to correlate the excited states in the molecules of benzaldehyde and halo substituted benzaldehydes with those of benzene and the chage transfer states between the substituents and the benzene molecule. The results obtained are discussed in the present paper.

2. Procedure of Calculations and Results

The phenyl nucleus in benzaldehyde, substituted benzaldehyde and benzoyl halide molecules is considered as a regular hexagonal ring. The CHO, ClCO and CBrO groups and the substituent halogen atoms are taken to be co-planar with the phenyl ring. The structural parameters used for those molecules are shown in table 1. Benzaldehyde has been considered as an eight electron—eight molecular orbital system while each of the substituted benzaldehydes and benzoyl halides is represented by a ten electron—nine molecular orbital system;

the halogen atom contributing two π-electrons in each case. In the case of ortho- and meta- substituted benzaldehydes both cis and trans configurations of the aldehyde group with respect to the halogen atom have been considered.

The molecular orbitals (ϕ_c) which are linear combinations of the π-orbitals (χ_μ) on the different atoms in the molecule are obtained together with their energies from the solutions of the usual Fock equations under the assumption of zero differential overlap. Following the suggestion of Carper and co-workers (1966, 1967) the elements of the Fock operator F are taken in the slightly modified form as

$$F_{\mu\mu} = (\tfrac{1}{2}P_{\mu\mu} - N_\mu)(\mu\mu\,|\,\mu\mu) + \sum_{\nu\neq\mu} (P_{\nu\nu} - N_\nu)(\mu\mu\,|\,\nu\nu)$$

and

$$F_{\mu\nu} = \beta_{\mu\nu} - \tfrac{1}{2}P_{\mu\nu}\,(\mu\mu\,|\,\nu\nu)_{(\mu\neq\nu)}$$

where N_μ is the number of π-electrons contributed by the μth atom and the other terms have their usual meanings.

The value of the resonance integral $\beta_c = 0$ obtained by using Kon's (1955) formula and those of the parameters $(\mu\mu\,|\,\mu\mu)$ and $\beta_{\mu\nu}$ taken from published literature values and are shown in table 1. The two electron, two centre integrals $(\mu\mu\,|\,\nu\nu)$ have been evaluated from Mataga's (1957) empirical relation.

Table 1. Structural and other parameters used with the different molecules.

r(C–C) ring	1.39Å[a]	(CC|CC)	10.959 ev[d]
r(C–C)	1.46Å[a]	(00|00)	15.230 ev[e]
r(C = 0)	1.22Å[a]	(ClCl|ClCl)	11.880 ev[b]
r(C–Cl)	1.69Å[b]	(BrB|BrBr)	11.460 ev[b]
r(C–Br,	1.86Å[b]	β(C–C) ring	−2.371 ev[d]
∠(C–C = 0)	120°[a]	β(C–C)	−1.68 ev[f]
∠(C–C–Cl)	118°[c]	β(C = 0)	−2.671 ev*
∠(C–C–Br)	115°[c]	β(C–Cl)	−3.620 ev[b]
		β(C–Br)	−3.450 ev[b]

* Calculated by Kon's (1955) formula;
(*a*) Inuzuka & Yokota (1965); (*b*) Russell *et al* (1967); (*c*) Khan & Jonathan (1969); (*d*) Knowlton & Carper (1966); (*e*) Hinze & Jaffe (1962); (*f*) Pariser & Parr (1953).

The singlet excitation energies, the corresponding oscillator strengths, the π-electron ionisation potential together with the singlet state functions have been calculated using the usual methods. The calculated values along with the corresponding experimental values wherever available are given in tables 2 and 3.

Table 2. Calculated and experimental transition energies, oscillator strengths and ionization potential of benzlandehyde

	Experimental	Calculated		
		Blood & Peradejordi (1962)	Inuzuka & Yokota (1965)	Present author *SCFMO*
Transition energies in ev[a]	4.50	4.69	4.77	4.69
	5.32	5.39	5.03	5.51
	6.36	6.48	6.31	6.37
		6.88	6.79	6.49
Oscillator strengths[a]	0.026		0.017	0.003
	0.290		0.066	0.362
	0.450		1.02	0.432
				0.602
Ionization potential in ev[b]	9.80		12.05	10.14

(*a*) Inuzuka & Yokota (1965); (*b*) Baker *et al* (1968).

The correlation of the different excited states in each of the benzaldehyde and substituted benzladehyde molecules with those of benzene and charge transfer states has been made following the method suggested by Baba *et al* (1969). The SCFMOs of the carbonyl group and their energies have been calculated by using the relevant parameters given in table 1. In these caclculations the contributions from doubly excited configurations were neglected. Some representative results are shown in table 4.

3. Discussion

Transition energies, oscillator strengths and ionisation potentials

It is seen from table 2 that the calculated values of the transition energies in the case of benzladehyde are in good agreement with the values given by Bloor & Peradejordi (1962) and fairly agrees with the experimental values given by Inuzuka & Yokota (1965). Also, the calculated *f*-values and ionization potential compare favourably with the corresponding experimental values.

For the para-, chloro- and para-bromo benzaldehydes (table 3) the calculated transitions energy values are in fair agreement with the experimental results. But the ionization potentials are lower than those given for these two molecules by Baker *et al* (1968). Calculations for para chlorobenzaldehyde were also carried out using the set of parameters suggested by Clark & Emsley (1967). In that case, though the ionization potential 9·66 ev obtained is closer to the experimental value 9·83 ev, the calculated values of the different transition energies are considerably higher than the experimental ones. For the ortho- and meta-substituted halobenzaldehyde molecules the agreement between the calculated and experimental results for the different state energies is satisfactory while in

the case of benzoyl halides (table 3) the calculated values of the state energies always remain higher than the corresponding experimental values reported by Sashidhar (1971) but the *f*-values are of the right order of magnitude.

Table 3. Calculated and experimental transition energies, oscillator strengths and ionization potential ain halo substituted benzladehydes and benzoyl halides

	Transition energies in ev.		Oscillator strengths		Ionization potential in e	
	Calc.	Expt.	Calc.	Expt.[e]	Calc.	Expt.[f]
Para chloro-benzyl-dehydo	4.49	4.35[b]	0.043			
	(4.63)		(0.002)			
	4.86	4.84[c]	0.564			
	(5.25)		(0.460)		8.88	9.83
	6.12	5.90[c]	0.393		(9.67)	
	(6.26)		(0.465)			
	6.49		0.108			
	(6.42)		(0.387)			
Para bromo-benzal-dehydo	4.49	4.34[b]	0.040			
	4.85	4.90[d]	0.589		8.85	9.60
	6.11		0.397			
	6.251		0.094			
Benzoyl chloride	4.74	4.30[c]	0.001	0.018		
	5.41	5.10[c]	0.245	0.198	9.54	
	6.09		0.095	—		
	6.11		0.011	—		
Benzoyl bromide	4.74	4.30[c]	0.001	0.008		
	5.41	5.10[c]	0.242	0.128		
	6.02		0.089	—	9.51	
	6.09		0.013	—		

Figures within paranthesses are the results calculated using Clark & Emsley's (1967) paramoter.

(*a*) Padhye & Viladkar (1961); (*b*) Dearden & Forbes (1958); (*c*) Doub & Vandenbelt (1955); (*d*) Jaiswal & Sharma (1963); (*e*) Sashidar (1971); (*f*) Baker *et al* (1968).

Correlation of excited states

It is seen from table 4 that the results obtained in the case of benzladehyde indicate that the first absorption band in this molecule may be correlated with the shifted α-band of benzene. For the higher energy states of the molecule none of the excited benzene or charge transfer states predominates. In the case of para-, meta- and ortho- halo substituted benzladehydes calculated results show that the contribution of the $\psi\alpha$ state of benzene to the first excited state in the respective molecules is much less than that in benzaldehyde and this contribution decreases in the order para < meta < ortho. Particularly, in the case of ortho substituted benzladehyde molecules the first excited state consists of such a low proportion of the $\psi\alpha$ state of benzene that it is not reasonable to assign this band to the shifted α-benzenoid band. Further, from table 4 it is

seen that in the states corresponding to higher transition energies in each of the substituted benzaldehyde molecules the different excited states of benzene and the charge transfer states become so thoroughly mixed up that it is not possible to assign these band systems to any particular transition.

Table 4. Correlation of the excited states of benzaldehyde and isomeric chlorobenzaldehydes with those of benzene and intramolecular charge transfer states

Energy state	Molecule	States of benzene					Charge transfer states*		
		ψ ground	ψ_α	ψ_p	ψ_β	ψ_β	T^A	T^D	$T_A{}^D$
	Benzaldehyde	—	86.00	—	—	—	8.20	—	—
	Para chloro benzaldehyde.	—	66.00				3.27	9.25	
1st	Meta chloro benzaldehyde (cis).	—	47.50		—		10.80	6.60	2.45
	Ortho chloro benzaldehyde (cis).	—	39.40	—	—	—	16.64	6.75	6.15
	Benzaldehyde	—	—	39.60	8.25	—	36.20	—	—
	Para chloro benzaldehyde.	7.23	—	20.70	6.64	—	29.00	3.62	5.80
2nd	Meta chloro benzladehyde (cis).	—	5.54	31.00	—	—	20.60	4.23	—
	Ortho chloro benzladehyde (cis).	6.85	19.30	19.20	—	—	18.30	2.90	4.56
	Benzaldehyde	—	3.62	13.40	4.36	32.00	33.70	—	—
	Para chloro benzaldehyde.			4.62	—	32.20	32.00	5.00	—
3rd	Meta chloro benzaldehyde (cis).	2.64	—	—	14.20	7.26	28.98	2.90	—
	Ortho chloro benzaldehyde (cis).	—	9.13	30.00	—	—	20.40	—	8.27

* T^A, T^D, $T_A{}^D$ indicate respectively the charge transfer states between benzene and carbonyl, chlorine and benzene and chlorine and carbonyl.

From the above discussions it is concluded that it may not be reasonable to correlate the different absorption band systems of benzaldehyde and substituted benzladehyde molecules with the benzenoid and intramolecular charge transfer bands. It will be more realistic to consider these bands as originating from transitions from the ground state to different excited states arising from the total π-electron configuration of the respective molcules

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